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(54) METHOD OF MANUFACTURING METALLIC PLATINUM POWDER

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## PATENT SPECIFICATION

1. Title of the Invention: Method of Manufacturing Metallic Platinum Powder

2. Claims:

A method of manufacturing a metallic platinum powder by adding a reducing agent solution to a metallic platinum complex solution and mixing the components, said method being characterized by the fact that after mixing, the mixed solution is subjected to stirring under the effect of ultrasonic waves.

3. Detailed Description of the Invention

The present invention relates to a method of manufacturing a metallic platinum powder from a metallic platinum complex solution for use as a catalyst.

Heretofore, it has been known to utilize various active precious metals as catalysts. Since precious metals are very expensive, in order to decrease the cost of the catalyst, it is necessary to reduce the amount of the precious metal used therein.

In order to achieve the above objective, it requires to produce a precious-metal powder with increased specific area and to provide uniform distribution of the powder particles on a catalyst carrier.

For example, known in the art is an electrode of a fuel cell that utilizes a catalyst in the form of a precious metal. Known methods often used for the manufacture of fuel-cell electrodes consist of impregnating a carbon powder that constitutes a carrier in a metal salt solution, conducting a heat-treatment

operation in a reducing atmosphere or in an activating atmosphere, and then subjecting, the appropriately bonded carbon powder particles carrying metal powder particles activated by the above treatment and distributed over its surface, to a forming process.

In other words, the above method consists only of impregnation of a carbon powder with a metal salt. That is, the process consists only of adsorption of metal ions or metal-complex ions and does not involve any electrochemical activation. And even if it involves the electrochemical activation, an indispensable condition of such a process is activation with the use of reduction that in majority of cases results in low activity. The conventional method is carried out in a reducing atmosphere with heat treatment at about 330°C and with activation. However, since in the above method heat treatment is carried out in a reducing atmosphere (e.g., in hydrogen), the process involves complicated operations and the use of large-scale equipment. Furthermore, heating causes growth or aggregation of metal particles and thus leads to non-uniform distribution. This creates unfavorable conditions for catalysis.

In order to eliminate the above drawbacks of the known process, it is recommended to conduct reduction in a liquid phase. Reduction in a liquid phase offers the following advantages:

- (a) Metal powder particles have more uniform distribution and a smaller size because, in a liquid phase, ions of independent complexes or ions of complexes adsorbed on the surface of a carbon powder carrier are more uniformly distributed;
- (b) The temperature is lower than in a gaseous phase, and therefore more difficult conditions are created for growth and aggregation of particles;
- (c) The production equipment and methods of operation are simple.

A method of liquid-phase reduction consists of mixing a metallic platinum complex solution with a solution of a reducing agent (e.g., formate or a formaldehyde solution), and then stirring the components. In order to accelerate the process, it should be accompanied by heating. However, since heating promotes growth of the metallic particles, the particles obtained by the known liquid-phase reduction method are obtained with a large diameter. Therefore, even though the thus obtained particles can be used for manufacturing

electrodes, because of a large diameter of particles, the above method cannot provide a powder of good characteristics.

The present invention is aimed at a solution of the problems inherent in the known liquid-phase method and consists of manufacturing a metallic platinum powder by adding a reducing agent solution to a metallic platinum complex solution, mixing the components, and then subjecting the mixed solution to stirring under the effect of ultrasonic waves. As a result, it becomes possible to obtain a fine platinum powder at room temperature and during a short period of time.

The authors have found that in contrast to a conventional macro stirring, the use of ultrasonic waves causes in the above reaction a specific effect of microstirring. Thus the authors arrived at the present invention.

In particular, it can be anticipated that when metallic platinum reduction occurs under conditions of ultrasonic stirring, the speed of the reaction will grow due to increase of collisions between particles of the reducing agent and particles of the platinum complex. Furthermore, the micron-level stirring will promote more uniform and increased development of crystals in the reaction system. Therefore, one can expect that upon completion of the reaction, the particles will have more uniform distribution and super-fine dimensions.

With ultrasonic stirring, the reaction can practically be carried out at room temperature and with increased speed. A comparison of the method of the invention with comparative examples that correspond to the known method of liquid-phase reduction at room temperature is given in Fig. 1 that shows reaction time versus production efficiency. It can be seen from this drawing that in the method of the invention the reaction speed is much higher than in the known method. For example, metallic platinum particles produced with the use of the ultrasonic-stirring method acquire BET-specific surface area equal to  $80 \text{ m}^2/\text{g}$ , which is three times greater than  $25 \text{ m}^2/\text{g}$  achieved by the known method. Average particle diameter measured by an X-ray method was much smaller and was within the range of 50 to 80 Å for the method of the invention and within the range of 120 to 180 Å for the known method.

Observation showed that reduced metallic platinum particles obtained by adding a reducing agent solution to a metallic platinum complex solution in combination with the addition of a catalytic carrier for adsorption on the surface of the carrier with simultaneous stirring of the components under the effect of ultrasonic waves, have a very uniform distribution on the carrier.

The invention will be further described with reference to practical examples.

#### Practical Example 1

A solution of a hexachloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) [subscripts are illegible – tr. note] in an amount of 0.1 M/l was added to activated carbon, and the components were stirred for 1 hour. The mixture was then combined with 150  $\text{cm}^3$  of a 10% sodium formate, and the platinum complex ions were reduced by subjecting the mixture to 3-hour mixing in an ultrasonic stirrer at 55 KHz. Observation of the resulting product under an electronic microscope confirmed the platinum particles on the activated carbon have uniform distribution of. X-ray measurement showed that particles have diameters within the range of 50 to 80 Å.

#### Practical Example 2

A solution of a hexachloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) [subscripts are illegible – tr. note] in an amount of 0.1 M/l was added to 150  $\text{cm}^3$  of a 10% solution of sodium formate while the components were stirred. The mixture was transferred to an ultrasonic stirrer, treated there for 3 hours, and then combined with activated carbon. Prior to addition of the activated carbon, the platinum particles were sampled and checked by the BET method. The measurements showed that the particles have specific surface area of 80  $\text{m}^2/\text{g}$ .

The following description relates to explanation of the effect obtained by using the metallic platinum particles as a catalyst.

A platinum powder produced in Practical Example 1 or Practical Example 2 uniformly distributed on the surface of activated carbon was combined with 50 wt.% of a tetrafluoroethylene suspension. The obtained mixture was spread

over the surface of a carbon sheet, formed into an electrode, and the electrode was assembled with a fuel cell. A unit cell of the obtained fuel cell had dimensions of 20 x 20 cm, and the construction comprised an electrolyte-containing layer sandwiched between the fuel electrode and an air electrode. The air electrode contained 0.7 mg/cm of platinum. The electrolyte-containing layer was made of a polymeric non-woven cloth impregnated in a phosphoric acid. Both electrodes were supplied with hydrogen and oxygen. Characteristics of the aforementioned fuel cell are shown in Fig. 2. This drawing shows a graph in which a cell voltage is plotted on the ordinate axis, and current density is plotted on the abscissa axis. A characteristic of the cell of the invention is shown by curve A, while a characteristic of the cell produced by a conventional method is shown by curve B. It can be seen that the cell of the invention has better characteristic than the cell produced by the known method.

Due to a smaller size of the particles and uniform distribution, the aforementioned fuel-battery electrode catalyst of the invention could be produced with a lower weight of the used platinum, and the electrode manufactured with the use of this platinum powder showed better catalytic action than in the case of the prior-art example.

Examples 1 and 2 described the use of platinum complex ions. However, the same effect can be achieved with the use of ions other than those of platinum complex, e.g., ions of palladium, ruthenium, iridium, or osmium may be used for the same purpose. Furthermore, hydrazine formaldehyde can be used instead sodium formate as a reducing agent.

#### 4. Brief Description of the Drawings

Fig. 1 is a graph illustrating time versus production efficiency of the platinum powder of the invention. Fig. 2 is a graph that shows characteristics of the fuel cell produced with the use of the platinum powder of the invention.

FIG. 1

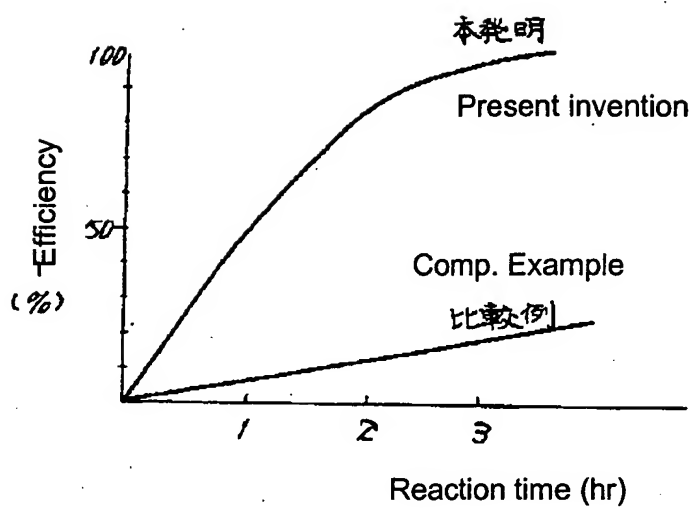


FIG. 2

